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CERAMIC WITH A LOW TCLE FOR DEPOSITION OF PROTECTIVE COATINGS MADE OF Nb_2O_5

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The thermal expansion of mullite-cordierite, mullite, and quartz ceramics used in production of materials with a protective Nb_2O_5 coating is investigated. It is demonstrated that fused quartz glass and quartz ceramics not containing the cristobalite phase are the closest to Nb_2O_5 in their thermal expansion. Variable-composition alloys $(Nb_2O_5)_x - (SiO_2)_{1-x}$ have intermediate TCLEs and can serve to compensate stresses caused by the discrepancy between the coating and the quartz ceramic substrate.

Protective coatings deposited on different structural materials find wide application in various spheres of science and engineering. Special attention is focused on ceramic coatings due to their resistance to the effects of high temperatures, aggressive media, and abrasive wear. It is known [1] that by applying a ceramic coating to a metallic substrate with a difference between the TCLEs of the coating and the substrate up to $(6 - 7) \times 10^{-6}$ K^{-1}, it is possible to produce a coating withstanding up to 7000 thermal cycles with a heating rate up to 1125 K/min and subsequent forced cooling to 250°C. To achieve this, researchers, as a rule, create intermediate layers between the base and the coating using materials with intermediate TCLE values.

Thermal expansion is a thermophysical characteristic of materials that depends mainly on the arrangement of atoms in the crystal lattice and the type of interatomic bonds, In the case of oriented monocrystalline grains (an oriented texture) the thermal expansion of ceramics may be influenced by the spatial anisotropy of the thermal expansion of the crystal lattice. In some materials thermal expansion may also depend on the formation of an extended microcrack structure [2]. Consequently, the thermal expansion of ceramics significantly depends on the method of its production.

Coatings made of Nb_2O_5 fused on a ceramic substrate find application in the production of containers and construction products used in the production of high-purity niobium and tantalum compounds. In the production of ceramics with protective coatings it is essential to select appropriate materials for the ceramic base. The authors in [3] propose such heat-resistant materials as mullite, mullite-cordierite, and quartz ceramics that exhibited sufficient resistance in the process of applying coatings and in heat-resistance tests of samples with a deposited Nb_2O_5 coating. The most technologically suitable material for the base was quartz ceramics, which was used to produce prototype containers for chemicothermal treatment of high-purity niobium compounds. It is known that the reliability and durability of products with a protective coating to a large extent depend on the ability to lower thermal stresses arising due to the discrepancy between the TCLEs of the base and the coating.

We studied the temperature dependences of the relative elongation of ceramic materials of the base (mullite, mullite-cordierite, and quartz ceramics), materials forming intermediate layers (alloys of the $Nb_2O_5 - SiO_2$ system), and materials for the coating (fused Nb_2O_5).

The ceramic articles considered do not experience such intense thermal loads as metallic parts with ceramic coatings [1]. However, the thickness of coatings on metals is a few microns, whereas protective coatings on ceramic containers need to be hundreds of microns up to 1.5 – 2.0 mm thick. It is obvious that the heat resistance of coated ceramic samples decreases in inverse proportion to the coating thickness, and the possibility of compensating stresses in the nonplastic ceramic substrate is significantly lower than in metal alloys. Therefore, a correct selection of the composition and properties of the intermediate layer is of critical significance in depositing ceramic coatings on ceramic substrates.

The measurements of temperature dependences of the relative elongation of ceramic samples were carried out in air using a DKV-5A automatic quartz dilatometer according to the differential method with a reference standard in the form of a quartz glass rod in the temperature interval of 20 – 825°C. The duration of heating is 2 h 30 min. The standard length of the samples is 50 ± 3 mm with a cross-section of 5 × 5 mm (± 0.5 mm). The ultimate error in measuring temperature is not more than 3.0°C. The error of measuring

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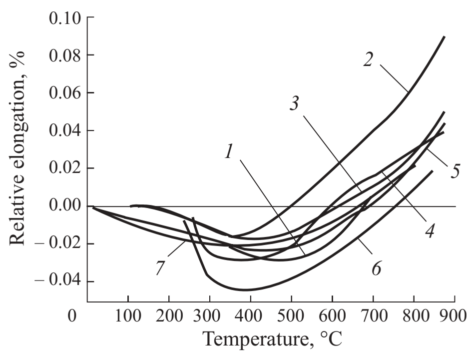

Fig. 1. Temperature dependences of relative elongation of Nb_2O_5 ceramic samples according to reference data from [4] (curves *1* – *6*) and the present study (curve *7*): *1*) 99.6% Nb_2O_5, residual Ta_2O_5, firing at 1455°C; *2*) the same, heating for 2 h at 1315°C, cooling in the furnace; *3*) the same, heating for 2 h at 1370°C, cooling in the furnace; *4*) the same, heating for 2 h at 1315°C, cooling in air; *5*) the same, heating for 2 h at 1370°C, cooling in air; *6*) the same, at 1370°C, cooling the furnace, repeated heating for 100 h at 1200°C, cooling in the furnace; *7*) sample of Nb_2O_5 of grade OSCh8-2 obtained by melting in the optical furnace.

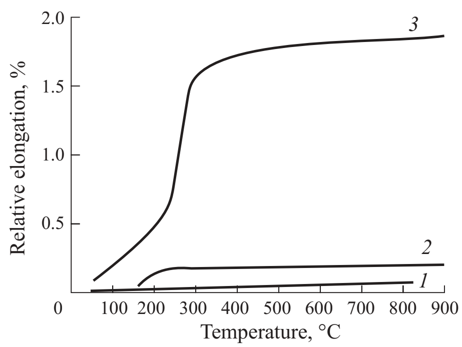

Fig. 2. Temperature dependence of the relative elongation of samples based on silicon dioxide: *1*) melted quartz glass; *2*) quartz ceramics of porosity 10% obtained by casting, annealing at 1350°C for 1 h; *3*) reference standard: cristobalite.

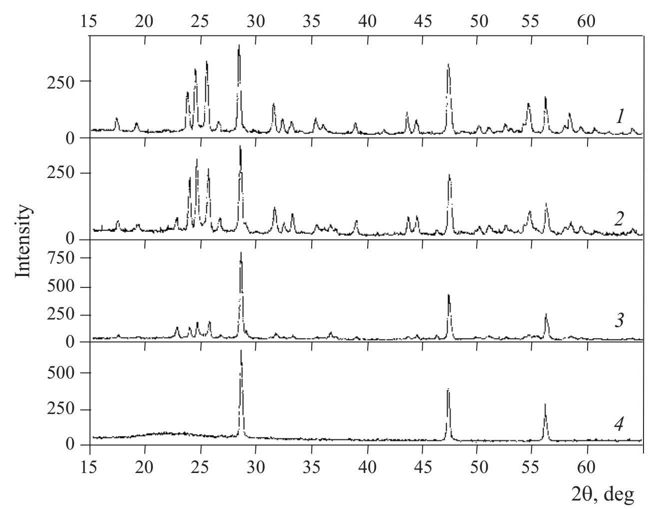

Fig. 3. Diffraction patterns of intermediate compositions of alloys in the system $(Nb_2O_5)_x – (SiO_2)_{1-x}$: *1*) $80Nb_2O_5 – 20SiO_2$; *2*) $60Nb_2O_5 – 40SiO_2$; *3*) $40Nb_2O_5 – 60SiO_2$; *4*) reference standard: quartz.

the TCLE in the temperature interval of 20 – 300°C is not more than 1.5×10^{-7} K^{-1} and in the interval of 20 – 100°C not more than 3×10^{-7} K^{-1}.

The batch for making samples was prepared by mixing Nb_2O_5 powder of grade "OSCh8-2" ("extra pure") and quartz glass powder. The batch was used to melt bars in an optical furnace, after which samples of size 5 × 5 × 50 mm were cut out from these bars to measure the relative elongation.

For reference purposes, the temperature dependences of the relative elongation was measured as well for samples cut out from melted Nb_2O_5 bars, samples of mullite ceramics developed by IPM of the National Academy of Sciences of Ukraine, mullite-cordierite ceramics developed at the UKRNIIFP Institute, and quartz ceramics with porosity 18 and 23% developed at the Podolsk Works of Refractory Products. Such quartz ceramics was used in [2] to produce containers with protective coatings made of Nb_2O_5.

The temperature dependence of the relative elongation of Nb_2O_5 ceramic samples subjected to different heat-treatment schedules is shown in Fig. 1. A typical feature of all samples based on Nb_2O_5 is the presence of a segment with a negative temperature elongation (up to 0.04%) within the temperature interval from 200 to 600 – 750°C. The value of the deviation into the negative value range depends on the duration and temperature of sintering ceramic and on the cooling conditions. The temperature dependence of the relative elongation of the fused Nb_2O_5 sample (the data of the present study) occupies an intermediate position, whereas the negative value range lies within a temperature interval up to 700°C and does not have sharp variations. The negative elongation can reach 0.02%. Hence it can be inferred that a more homogeneous crystalline structure is formed in melting ceramic bars from Nb_2O_5.

For silicon diopside as well the temperature dependence of relative elongation significantly depends on the phase composition and thermal treatment schedules (Fig. 2) [5].

It is known that Nb_2O_5 and SiO_2 do not form solid solutions [6] and their alloys at a state of equilibrium consist of a mixture of Nb_2O_5 crystals and the tridimite phase SiO_2. In rapid cooling of bars the tridimite phase does not have time for crystallization; therefore, alloys $(Nb_2O_5)_x – (SiO_2)_{1-x}$ will consist of a mixture of Nb_2O_5 crystals and quartz glass, which is supported by the results of x-ray phase analysis (Fig. 3).

The diffraction patterns were recorded using a DRON-3M set with a graphite monochromator on a diaphragmed beam in CuK_α radiation using discrete angle scanning with a step of $2\theta = 0.05°$. Silicon was used as the internal reference standard. Niobium pentoxide identified in samples with a high content of Nb_2O_5 had a monoclinic lattice (a = 2.0381 nm, b = 0.38249 nm, c = 1.9368 nm, β = 115.694;

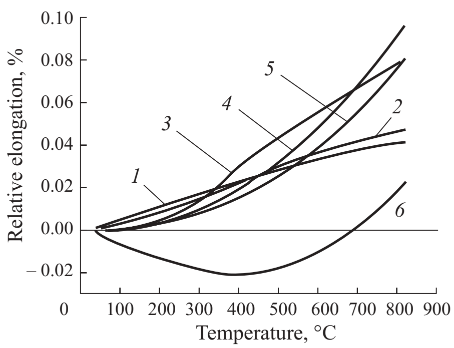

Fig. 4. Dependence of relative elongation of fused samples of ceramics $(Nb_2O_5)_x - (SiO_2)_{1-x}$: *1*) fused quartz glass [3]; *2*) $20Nb_2O_5 - 80SiO_2$; *3*) $40Nb_2O_5 - 60SiO_2$; *4*) $60Nb_2O_5 - 40SiO_2$; *5*) $80Nb_2O_5 - 20SiO_2$; *6*) sample of Nb_2O_5 of grade OSCh8-2 obtained by melting in optical furnace.

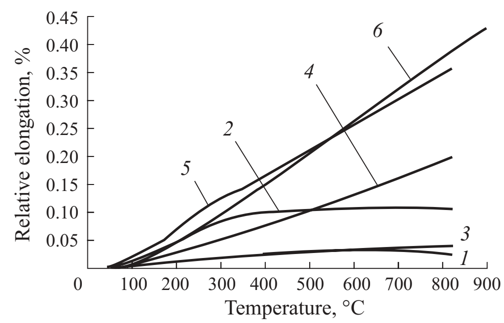

Fig. 5. Temperature dependence of relative elongation of ceramic samples: *1*) quartz ceramics of porosity 23% (Podolsk Works); *2*) quartz ceramics of porosity 18% (Podolsk Works); *3*) melted quartz glass [5]; *4*) mullite ceramics (IPM NAS of Ukraine); *5*) mullite-cordierite ceramics (UKRNIIFP); *6*) mullite [4].

ICDD database). As the content of SiO_2 increases, beside the monoclinic phase of niobium pentoxide, Nb_2O_5 with a rhombic lattice is registered ($a = 0.6168$ nm, $b = 2.9312$ nm, $c = 0.3938$ nm; ICDD database). Silicon dioxide in all samples remains in the amorphous state.

For a deeper understanding of the behavior of the intermediate layers in fusing and service of quartz ceramic products with protective Nb_2O_5 coating, we measured the temperature dependence of the relative elongation of samples of the following compositions (here and elsewhere wt.%): $20Nb_2O_5 - 80SiO_2$, $40Nb_2O_5 - 60SiO_2$, $60Nb_2O_5 - 40SiO_2$, and $80Nb_2O_5 - 20SiO_2$. Figure 4 shows the dependences of the relative elongation of fused ceramic samples of compositions $(Nb_2O_5)_x - (SiO_2)_{1-x}$.

The following conclusions can be made analyzing the plots in Figs. 1 and 4:

– the fused sample of pure Nb_2O_5 (grade OSCh8-2) is characterized by negative values of relative elongation in the temperature range up to 670°C;

– in the temperature interval from 25 to 350 – 400°C the TCLE of Nb_2O_5 has negative values; on further increase in temperature the TCLE becomes positive;

– fusing Nb_2O_5 together with quartz glass leads to the disappearance of the temperature range of negative values of relative elongation;

– as the SiO_2 content grows from 60 to 80%, variations in relative elongation and its absolute values approach the respective values for fused quartz glass;

– the transition of temperature dependences of relative elongation from the negative range to the positive range after adding silica to Nb_2O_5 may be accounted for by the healing of microcracks or by a more random orientation of Nb_2O_5 grains in crystallization in a viscous silicate melt.

Figure 5 shows temperature dependences of the relative elongation of ceramic samples. As can be seen, the temperature dependence of the relative elongation of quartz ceramics with porosity 23% is close to the temperature dependence of quartz glass. The higher relative elongation values registered in quartz ceramics with porosity 18% are due to the increased content of the cristobalite phase, which is formed with increased sintering temperature and increased duration of sintering of quartz ceramics needed to decrease porosity.

The results obtained suggest the following conclusions:

– the thermal expansion of fused Nb_2O_5 resembles most that of fused quartz glass and quartz ceramics in the absence of the cristobalite phase;

– the eutectic alloys of the compositions $(Nb_2O_5)_x - (SiO_2)_{1-x}$ formed in the intermediate layer between quartz ceramics and the Nb_2O_5 coating within an interval below 400 – 600°C have a lower TCLE than that of the underlying layers, and in the range above 400 – 600°C have a higher TCLE than that of the underlying layers; therefore, sign-change stresses may arise in the vicinity of the coating in heating.

– in general, variable-composition alloys $(Nb_2O_5)_x - (SiO_2)_{1-x}$ forming in the intermediate layer have intermediate TCLE values and can compensate the stresses caused by a discrepancy between the coating and the quartz ceramic substrate; quartz ceramics with porosity 23% is preferable with respect to its TCLE agreement.

All ceramic materials whose temperature expansion was analyzed in the present study exhibit relatively good heat resistance and can be used to develop ceramic products with a protective coating made of Nb_2O_5.

REFERENCES

1. M. Hoking, V. Vasantasri, and P. Sidki, *Metallic and Ceramic Coatings* [Russian translation], Mir, Moscow (2000).
2. M. F. Thomas and R. Stevens “Aluminium titanate — a literature review. Part 1: Microcracking phenomena,” *J. Br. Ceram. Soc.*, **88**, 144 – 151 (1989).
3. A. A. Frolov, “Ceramic materials for producing high-purity oxides of niobium and titanium,” *Steklo Keram.*, No. 7, 14 – 15 (1992).
4. R. E. Krzhizhanovskii and Z. Yu. Shtern, *Thermophysical Properties of Nonmetallic Materials, A Reference Book* [in Russian], Énergiya, Leningrad (1978).
5. Yu. E. Pivinskii and A. G. Romashin, *Quartz Ceramics* [in Russian], Metallurgiya, Moscow (1974).
6. N. A. Toropov, V. P. Barzakovskii, V. V. Lapin, and N. N. Kurala (eds.), *Phase Diagrams of Silicate Systems. Issue 1, Binary Systems* [in Russian], Nauka, Leningrad (1965).